**APPENDIX 4B
TEST CHEMISTRY**

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1 INTRODUCTION

The U.S. Army Project Manager for Non-Stockpile Chemical Materiel is developing a transportable system to treat recovered chemical warfare materiel (CWM). The first version of this system will be the Munitions Management Device, Version 1 (MMD-1), designed to treat non-explosively configured CWM. The MMD-1 will be used at remediation sites where non-stockpile CWM have been, or will be, found. Before the MMD-1 begins operation, it will be tested at Dugway Proving Ground, Utah, using simulated materiel and military munitions and Department of Transportation (DOT) cylinders containing chemical agents or industrial chemicals. The MMD-1 is designed to demilitarize various chemical agents and industrial chemicals. However, during this test phase, only three chemical agents and one industrial chemical will be processed.

The U.S. Army considers the demilitarization of the military substance in the MMD-1 a Adetoxification,@ since the process alters the chemical, physical, and toxicological properties to render the chemical agent or industrial chemical ineffective for use in weapons. The demilitarization process is also termed Aneutralization,@ which has been defined by the Army (AR 50-6, 1995) as the act of altering chemical, physical, and toxicological properties to render the chemical agent ineffective for use as intended. The product of neutralization has been defined as the Aneutralent,@ and the term Aneutralization reagent@ will be applied to the treatment liquids that will react with the CWM to cause the detoxification.

The chemical agents and industrial chemical that will be processed during the MMD-1 test are sulfur mustard (HD), nonpersistent nerve agent (GB), persistent nerve agent (VX), and the industrial chemical phosgene. This Appendix describes the important chemical properties of the chemical agents and industrial chemical that will be treated by the neutralizing reagents and their reactions.

A reagent reacts with the chemical agent or industrial chemical in the test item to convert the chemical fill to less toxic products that are not classified as CWM. However, these products may still present certain hazards to personnel or the environment. The detoxification reactions are discussed in detail in Sections 6 through 10. In addition to munitions and DOT cylinders containing chemical agent or industrial chemical phosgene, simulated equipment test hardware (SETH) will be used in the initial phase of the MMD-1 test. Some of the SETH may be filled with air, water, or methyl salicylate (MES), also known as wintergreen oil.

The physical and chemical properties data presented herein are based on Army documents (such as Field Manual (FM) 3-9; USARRADCOM USCSL, 1990), handbooks (Budavari, 1989; Dean, 1985; Perry and Green, 1984; Weast, 1988), manufacturers= technical information (Texaco Chemical, 1992; Union Carbide, 1965; Dow Chemical, 1995), material safety data sheets (Genium, 1985; Texaco Chemical, 1993; CRDEC USARMCD, 1991), and interviews with Edgewood Research, Development and Engineering Center (ERDEC) research personnel (MacIver, Procell, and Bartram, 1994b).

2   PHYSICAL AND CHEMICAL PROPERTIES OF CHEMICAL AGENTS

The structural formulas and physical and chemical properties of sulfur mustard agents (H, HD, and HS), and GB and VX are shown in **Figures 4B-1** and **4B-2**. These chemical agents are liquids at room temperature, and contain a few to several percent of impurities (munition-grade). Only the major impurities, which are chemically similar to the chemical agents, are discussed in this Appendix. All the chemical agents except GB exhibit low solubility in water, and all react with alkali hypochlorites or alkalis in water or alcohols. GB is miscible with water.

Cl↵ CH₂↵ CH₂↵ S↵ CH₂↵ CH₂↵ Cl

<u>**Mustard, HD**</u> (H and HS are different abbreviations applied to this agent to designate purity)
bis-(2-chloroethyl) sulfide; CAS RN: 505-60-2
MW: 159.08.
Oily, amber to colorless liquid (b. p. greater than 442 F, greater than 228 C; HD decomposes near this temperature).
Odor: like garlic or horseradish.
Vapor pressure: low (0.09 mm at 86°F).
Density: 1.27 g/ml; 10.6 lb/gal.
Viscosity: 4.5 cP at 68°F (munitions-grade is often more viscous).
Freezing point: 55°F, 13°C.
Slightly soluble in water (0.9 parts/100 parts, by weight at 68°F).
Soluble in organic solvents such as chloroform, acetone, gasoline.
Reacts with oxidizing agents (peroxide, hypochlorite salts) to form sulfoxides and/or sulfones; reacts with alkali, ammonia, or amines to form substitution products.

Figure 4B-1. Mustard Formula and Properties
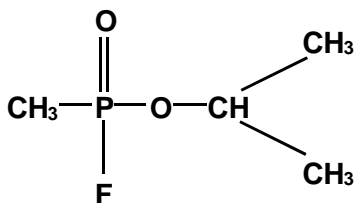
<u>**GB (Sarin)**</u>
isopropyl methylphosphonofluoridate
CAS RN: 107-44-8
MW: 140.09.
Colorless liquid (b. p. 304°F, 151°C).
Odor: almost none.
Vapor pressure: moderate (2.1 mm at 68°F).
Density: 1.102 g/ml; 9.2 lb/gal.
Viscosity: 1.92 cP (temperature not reported).
Freezing point: -69°F, -56°C.
Miscible with water.
Soluble in all organic solvents, including alcohols, gasoline, oils, and fats.
Reacts rapidly with strong alkali in aqueous and organic solutions to form sodium fluoride, or other fluoride salts, and a methylphosphonate; reacts slowly with water at pH less than 8.
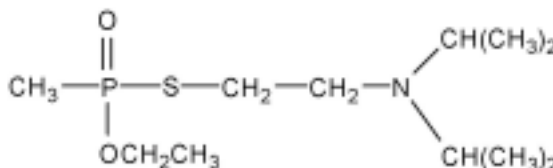
<u>**VX**</u>
O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate
CAS RN: 50782-69-9
MW: 267.36.
Colorless liquid (b. p. 568°F, 298°C - decomposes).
Odor: none.
Vapor pressure: very low (0.00033 mm at 68°F).
Density: 1.008 g/ml; 8.4 lb/gal.
Viscosity: 12.4 cP at 68°F, 4.42 cP at 122°F.
Freezing point: below -60°F, -51°C.
Solubility in water: 3 parts/100 parts by weight.
Soluble in most organic solvents, including alcohols, gasoline, oils, and fats.
Soluble in inorganic acids.
Reacts with strong alkali in aqueous and especially in organic solutions to form methylphosphonate salts, mercaptide salts, and other products that are very toxic; reacts very slowly with water.

Figure 4B-2. GB and VX Formulas and Properties

3 PHYSICAL AND CHEMICAL PROPERTIES OF PHOSGENE

Phosgene, is a highly volatile, reactive substance. Any substances that have been produced for use by military forces, but are not defined as "chemical agents" by the Army or treaty conventions, are classed as industrial chemicals. They are all available commercially. The structural formula and brief description of the properties of phosgene are shown in **Figure 4B-3**.
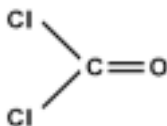
Phosgene, CG
carbonyl chloride; CAS RN: 75-44-5
MW: 98.92.
Colorless (if pure), liquefied gas
(b. p. 45.7^{o}F, 7.6^{o}C).
Odor: like new-mown hay.
Vapor pressure: 1,215 mm, 68°F (8.8 psig).
Density: 1.43 g/ml; 11.9 lb/gal.
Viscosity, liquid: 0.39 cP at 32°F.
Freezing point: -180°F, -118°C.
Slightly soluble in water, but it reacts to form hydrochloric acid and carbon dioxide.
Miscible with chloroform, acetone, and many other organic solvents. In alcohols, a reaction of phosgene and the alcohol will occur.
Reacts very rapidly with sodium hydroxide and other alkalis (sodium carbonate, lime, etc.), ammonia, and amines.

Figure 4B-3. Phosgene Formula and Properties

4 PHYSICAL AND CHEMICAL PROPERTIES OF NEUTRALIZATION REAGENTS, SIMULANTS, AND SOLVENTS

The reagents, dissolved in a solvent, convert chemical agents and industrial chemicals to less toxic substances by reactions that proceed rapidly at moderate temperatures. In some of these processes, the solvent participates in the chemical reaction (see Sections 6 through 9). Solvents ensure that the reagent and the products of the reactions are soluble. Because it was found most feasible to construct the MMD-1 from metal vessels, the reagent solution and the choice of metal (stainless steel) were chosen to avoid corrosion of the equipment. Consequently, the choice of suitable solvents is somewhat limited. The properties of the reagents, solvents, and simulants are shown in **Figures 4B-4** and **4B-5**.

Na⁺⁻OH
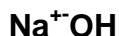
Sodium hydroxide
FW: 40.00.
CAS RN: 1310-73-2
White solid, flakes or pieces (available as 50% clear solution in water).
Odor: None, but irritates the nose.
Density: 2.13 g/ml (50%: 1.53 g/ml, 12.8 lb/gal).
Viscosity (50% solution): 100 cP at 68°F;
39 cP at 104°F.
Melting point: 604°F, 318°C.
Soluble in water, soluble in lower alcohols (methyl, ethyl, isopropyl, butyl, MEA); insoluble in benzene, gasoline, and ethers.
Reacts with acids, certain organic compounds such as chlorocarbons and nitro derivatives; absorbs carbon dioxide and water; attacks aluminum, zinc, and tin metals to form hydrogen gas (flammable).

Figure 4B-4. Sodium Hydroxide Detoxification Reagent

HO—CH₂CH₂—NH₂

MEA (monoethanolamine)
2-aminoethanol; CAS RN: 141-43-5
MW: 61.09.
Clear, somewhat viscous liquid (b. p. 339°F, 170.4°C).
Odor: Ammonia-like.
Vapor pressure: low (0.4 mm at 68°F).
Density: 1.018 g/ml, 8.49 lb/gal.
Viscosity: 24.1 cP at 68°F; 5.03cP at 140°F.
Freezing point: 50.5°F, 10.3°C.
Flashpoint: 201°F (94°C), LT Setaflash
Miscible with water, methanol, acetone; slightly soluble in benzene (0.6%), heptane (0.1%), and petroleum ether.
MEA is a hygroscopic substance: it absorbs water from humid air.
Reacts rapidly with active chlorine-containing compounds [sodium or calcium hypochlorite (bleach or HTH)], reacts with acids (examples: sulfuric acid, acetic acid), bifunctional organic compounds (examples: acrylonitrile, epichlorohydrin), and certain metals (examples: copper, galvanized iron); absorbs carbon dioxide.

Figure 4B-5. Monoethanolamine Detoxification Reagent/Solvent

5   DETOXIFYING SULFUR MUSTARD, HD

HD will be treated with monoethanolamine (MEA)-water solution to convert it to less toxic products. Crude or degraded mustard, mustard analogue (Q), or mixed mustards (HT) may be found in the tested munitions. These agent modifications are highly toxic, but they are also structurally similar to HD. The U.S. Army has demonstrated that Q, as an impurity in HD, will react with MEA (ERDEC, 1996a), and (2-chloroethylthio)ethyl ether (T) is expected to react because of its similar structure. The reaction of HD with MEA has been studied by the U.S. Army (see Brankowitz, 1978; Yurrow and Davis, 1982; MacIver et al., 1994a). In the presence of excess MEA and 10 percent water, the reaction proceeds at a moderate rate to form N-(2-hydroxyethyl)-thiomorpholine (HETM) as a major product; bis[2-(2-hydroxyethyl-amino)ethyl] sulfide (HEAES) and monoethanolamine hydrochloride (MEA·HCl) are also formed, as shown in **Figure 4B-6**.
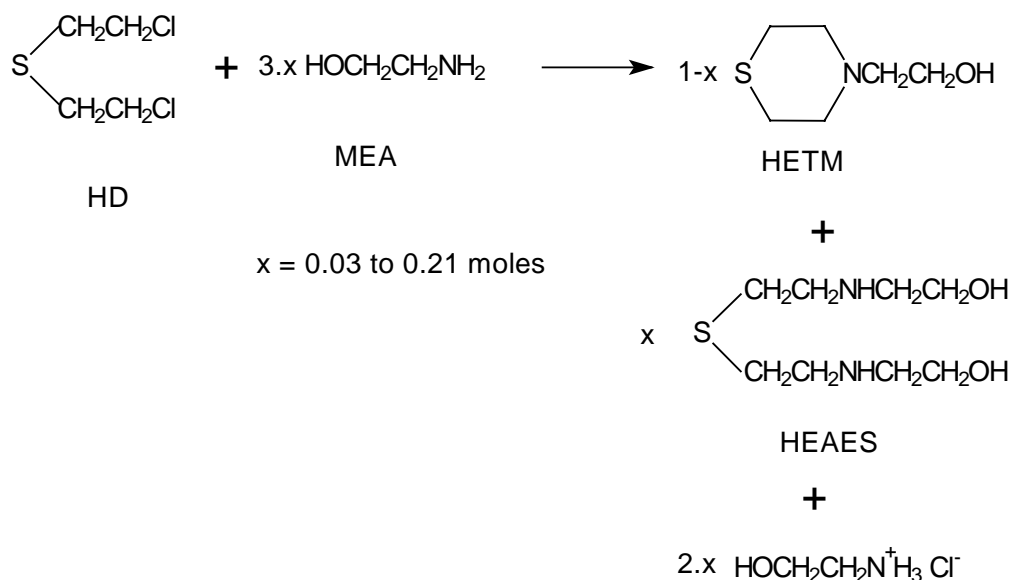

Figure 4B-6. Reaction of HD with MEA

Although the HD does not immediately dissolve in the solution (see Procell, 1995; Patel et al., 1995a), the HD reacts with the solvent mixture to form products that are all soluble in the neutralent along with impurities that are expected to be in the munitions grade HD. In this reaction, an excess of the reagent is used. As a result, the concentration of the chemical agent being detoxified will be characterized by a first-order rate of reaction; that is, the rate of chemical agent reaction depends only on its own concentration (at constant temperature), or the fractional life (usually the half-life) of the chemical agent will be constant. This first-order dependence of agent concentration with time can then be expressed by equation 4B-eq1, below.

instantaneous rate = k [agent]
[agent] = concentration of agent; k is the rate constant
At time, t:

$$\ln\left(\frac{[initial\ agent]}{[agent]}\right) > kt \qquad \textbf{(4B-eq1)}$$

For example, if one-half of the agent is converted in 2.5 minutes, three-quarters of the original amount of agent will convert in 5 minutes, seven-eighths in 7.5 minutes, etc. The graph shown in **Figure 4B-7** illustrates the change in concentration in any first-order reaction at constant temperature. In the example used above, the arbitrary unit in **Figure 4B-7** on the abscissa would equal 8.31 minutes or the rate constant would equal 0.28 minute[-1]. As shown in **Table 4B-1,** this rate constant was observed if 10 volume percent water is present and the temperature is a constant 158°F. The rates of most chemical reactions increase with increasing temperature, as found by Arrhenius, and the dependence of the rate is described by:

$$k > Ae^{-\frac{E}{RT}} \qquad \textbf{(4B-eq2)}$$

or

$$\ln k > \ln A . \left(\frac{E}{RT}\right) \qquad \textbf{(4B-eq3)}$$

In these equations, k = chemical rate constant, A = a constant (frequency factor), E = activation energy (Btu/lb-mole or cal/g-mole), R = ideal gas constant (1.9872 Btu/lb-mole/°Rankine or cal/g-mole/°Kelvin), and T = absolute temperature (°Rankine or °Kelvin, respectively).
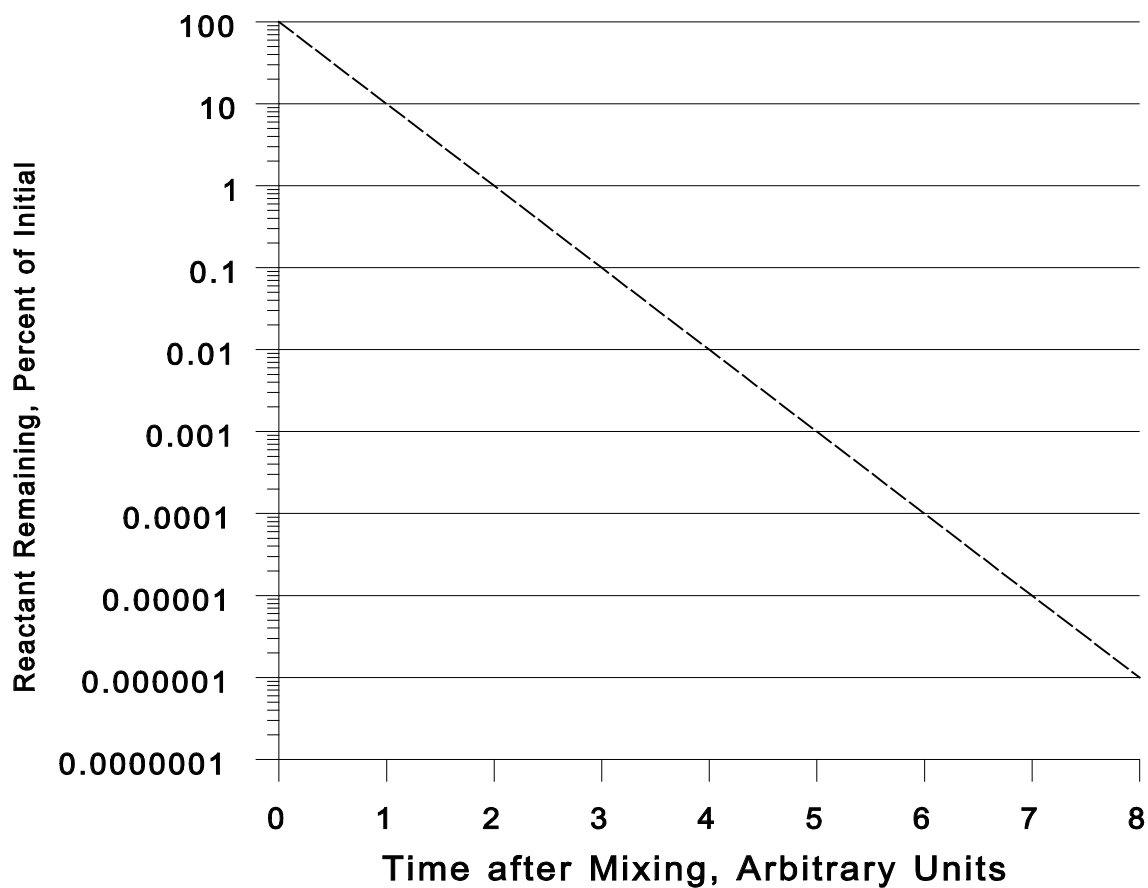
Figure 4B-7. General First-Order Reaction, Reactant Remaining at Any Time, Percent of Initial

The rate of the MEA/HD reaction was determined at various temperatures and at various concentrations of water in MEA (MacIver et al., 1994a). The process was found to be characterized by a first-order rate of reaction. The results also indicated that the rate of the reaction increases as more water is present, and it also increases with temperature. The derived results are shown in **Tables 4B-1 and 4B-2**. From the data at various temperatures, the activation energy was found to be 22.3 kcal/g-mole (MacIver et al., 1994b) in the 23 volume percent water/MEA solution. Later studies performed at different temperatures (Sneeringer, 1995; Patel, 1995a; Lindsay, 1995; ERDEC, 1996a) provided additional information. These later results show that the reaction at 86° to 91°F was not completed within 4 hours. Even after 21.7 hours, 92 mg/L of HD remained in the liquid (Lindsay, 1995), but the most recent laboratory results (ERDEC, 1996a) showed that if the reaction is started at 122°F nearly all of the HD can be neutralized within 4 hours. As shown in **Figure 4B-8** and **Table 4B-3,** 42.1 percent of the HD is converted in 6.3 minutes and 99.98 percent is converted 4 hours after mixing to leave only 17 parts per million (ppm) of HD remaining in the liquid (ERDEC, 1996a). A further reduction in the HD concentration occurred upon storing the mixture for several weeks, and no HD, above the detectable limit of 50 parts per billion (ppb), was found in the liquid.   The temperature in the above experiment rose to 175°F within 22 minutes and dropped below 100°F after 3 hours. This maximum reaction temperature is not expected in the MMD-1 system because either a higher ratio of reagent to HD will be used or the HD will be metered slowly into the heated reagent. As demonstrated by these laboratory results, the reagent will have to be heated to allow the reaction to proceed at an adequate rate. Heat can be added to the mixture from the heaters on the reagent storage and/or the liquid reactor vessel or by injecting steam into the mixture, which will be able to raise the temperature of the mixture to the required temperature. As the reaction proceeds, heat will be generated. The amount of heat generated by the reaction, in the absence of water, was measured (Brankowitz, 1978) and found to be 460.5 to 707.2 Btu/lb of HD consumed. MacIver et al. (1994a) found that 548.8 Btu/lb of HD was generated by the reaction when water was present at 140° to 217°F. From these data the amount of heat generated for tests of certain HD-containing munitions can be calculated, and the resulting temperature in the process can be estimated. For example, a standard HD 4.2 inch mortar round contains 6.25 lbs of agent that would generate 3431 Btu upon reaction with an excess of MEA/water. If 100 gallons of reagent were used, it can be estimated that the temperature of the mixture would increase by 6°F.   In the case of an M47 bomb, which contains 73 lbs of HD, the treatment with 200 gallons of MEA/water would generate 40,077 Btu, and it can be estimated that the amount of heat would raise the mixture=s temperature by 35°F. Since these temperature estimates ignore the fact that the metal of the MTV and LRV will also be heated by the reaction, the estimated temperature increases represent the maximums expected.

Table 4B-1. HD Reaction Rate Studies Effect of Water			Table 4B-2. HD Reaction Rate Studies Effect of Temperature (23% Water)		
Various Concentrations of Water in MEA at 158°F (70°C)			Rate of the MEA/HD Reaction at Various Temperatures with 23 vol. % water (1 volume of HD per 13 volumes of reagent)		
Water, vol%	Ratio HD:Reagent	Half-life of HD, minutes (rate const. k min^{-1})	Temperature, °F (°C)	Half-life of HD, minutes (rate const. k min^{-1})	
0	1:10	3.7 (0.187)	122 (50)	8.8 (0.079)	
10	1:11	2.5 (0.277)	140 (60)	2.5 (0.277)	
17	1:12	1.8 (0.385)	158 (70)	0.63-1.2(1.096-0.58)	
23	1:13	0.63-1.2(1.096-0.58)	176 (80)	0.61 (1.135)	
29	1:14	1.2 (0.58)	194 (90)	0.15 (4.604)	
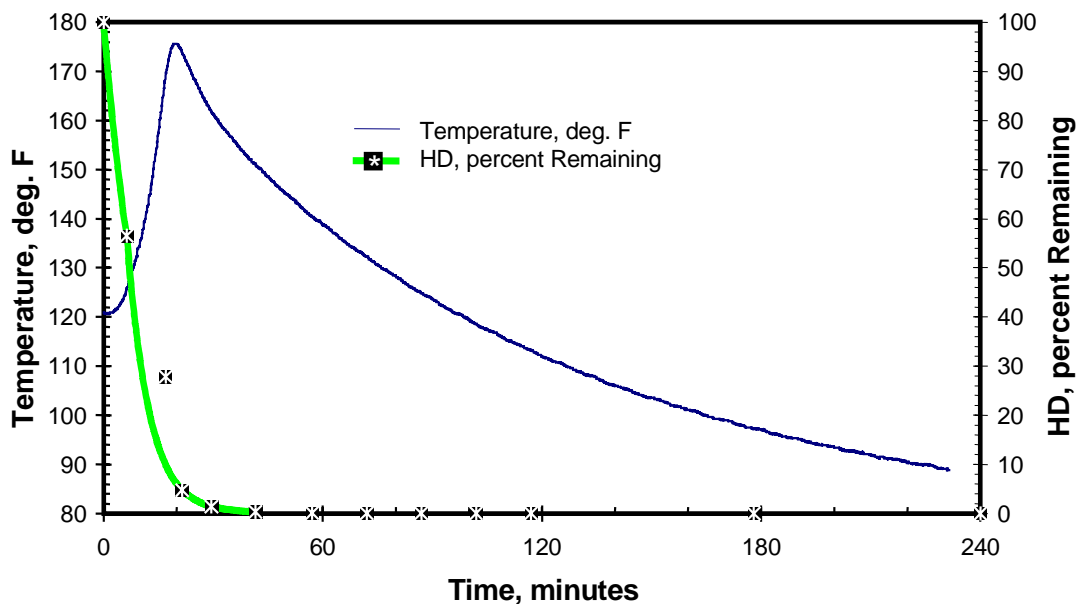
Figure 4B-8. Reaction of HD with MEA/Water, Temperature, and Agent Profiles

Table 4B-3. Reaction of HD with MEA/Water
Reaction Profile

Sample No.	Time after Start, Minutes	Conc. of HD, ppm	Amount of HD Remaining, Percent
	0	84,027[a]	100[a]
1	6.3	47,500	56.5
2	17.0	23,400	27.8
3	21.5	4,000	4.8
4	29.5	1,200	1.4
5	41.5	280	0.33
6	57.0	88	0.10
7	72.0	65	0.077
8	87.0	62	0.074
9	102.0	30	0.036
10	117.0	50	0.060
11	178.0	18	0.021
12	240.0	17	0.020

NOTE:

a   Calculated amount of HD charged to the reactor (weight percent times the assay of 92.8% HD).

In a series of three experiments, HD was mixed with MEA/water at 74° to 77°F in a jacketed reactor, stirred without heating for 2 hours, and then heated by pumping water at 130°F into the jacket. In all three experiments, the temperature rose to 150° to 152°F over the next 30 minutes. In the samples taken after 340 minutes from two of these experiments, it was found that the HD concentration was reduced to 64 to 108 mg/L. (ERDEC, 1996a). The sample from the third experiment was not analyzed on the day performed. The HD was found at levels of 0.06 to 0.32 mg/L after 24 hours of storage in the neutralent from two of these experiments, and 2 to 7 days later no HD could be found by analysis in the last sample from all three experiments. Because it was found that the gas chromatograph/mass spectrometer (GC/MS) method of analysis used could detect 0.05 mg/L HD, added to the neutralent, the analyst stated that the no-detection-results must be less than that value. As discussed in Section 10, analytical method improvement, to include precision and accuracy studies, are in progress.

The HD in the munitions or other containers in this test will be impure HD because of its original composition as manufactured and the degradation of the agent that has occurred upon storage. The results of recent analyses (ERDEC, 1996a) of munitions grade HD are shown in **Table 4B-4**. The major impurity was found to be agent Q [1,2-bis(2-chloroethylthio)ethane], also a known, highly toxic, chemical warfare agent. Mixtures of other 2-chloroethyl- and chloropropyl- and chlorobutyl- sulfides were also found. These latter materials are also vesicants, and they may also be neutralized by reaction with MEA. Chemical agent T was not found in these lots of HD, but it may be encountered in some munitions that are to be demilitarized in the MMD-1 system. Some older munitions have been manufactured to contain a mixture of agent H and agent T, designated as HT. Agent T is also expected to be neutralized by the MEA/water reagent. The 1,4-dithiane, along with 1,2-dichloroethane (EDC, or ethylene dichloride), can be formed from Agent Q during storage or processing. The EDC and 1,4-dithiane are not vesicants, but the EDC is classified as a toxic material by Resource Conservation and Recovery Act (RCRA) regulations. The EDC may also react with the MEA because only low concentrations of this material were in the HD neutralent (see **Appendix 4A**), but the 1,4-dithiane does not seem to react with the MEA. The experiments for the concentration of Q indicated that the concentration of Q was below the detection limit of 100 ppb in all cases. These analyses were performed after the neutralent had been removed from the reactor and stored at room temperature for 3 to 5 days. No agent T was found above its detection limit of 100 ppb, but no significant amount of T was present in the HD fed to the reactor.

1,4-dithiane was found at levels of 0.06 to 0.1 percent in the HD neutralent, consistent with the 1:10 dilution that occurs in the process (ERDEC, 1996a). Analyses of the neutralent from eight laboratory

Separate GC and nuclear magnetic resonance (NMR) methods of analyses were applied to the neutralents produced in the laboratory experiments to determine the bulk and trace level compositions (ERDEC, 1996a).

Table 4B-4.   Composition of Three Lots of Munitions Grade HD Used in the MEA/Water Neutralization Study

Component	Percent Found[a]
Agent HD	91.5-92.8[b]
Agent Q	5.7-7.3[b]
Other chlorinated sulfides (propyl, butyl, ethyl propyl, ethyl butyl)	1.8-2.8[b]
1,4-dithiane	0.6-1.0[b]
1,2-dichloroethane (EDC)	0.3-0.9[b]
Other impurites[c]	up to 0.6 [b]

NOTES:

a   Results from HD Technical report on three lots of HD (ERDEC, 1996a).

b   Values are in terms of area percent from GC analyses and do not represent exact weight or mole percent.

c   These impurities were found in only one lot of the three analyzed. They include chlorobenzene; 2-chloroethyl disulfides, trisulfides, and sulfoxides; and 1,4-thioxane.
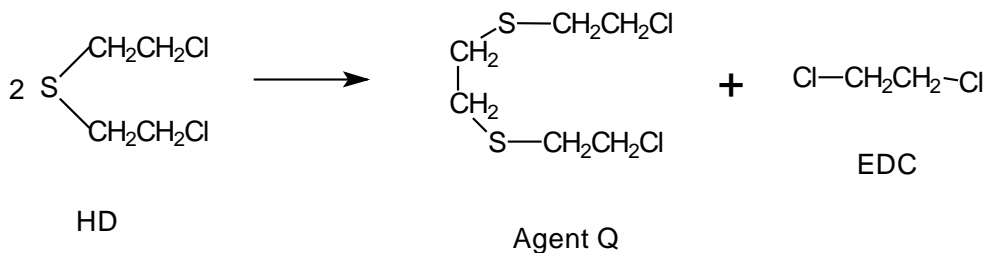
Attempts were made to chromatograph the mixture and determine the linear product, HEAES, and analogous products from agent Q and analogs. These substances could not be determined, as such, by chromatography, but they could be converted to trimethylsilyl (TMS) derivatives by treating the neutralent with bis(trimethylsilyl)trifluoroacetamide (BSTFA). The TMS derivatives could be separated chromatographically and the identity of the products was confirmed by the mass spectral determination made with a MS detector. In this manner, it was determined that HEAES, and the 1,2-[2-(2-hydroxyethylamino)ethylthio]ethane (MEA-Q, in **Figure 4B-9**) were present, but the quantities could not be determined because no authentic materials were available for calibration. The major product of the reaction, the thiomorpholine, HETM, was determined in the neutralent by quantitative GC, and quantitative ^{13}C NMR. This product was also detected by a liquid chromatography/mass spectrometry (LC/MS) method. The GC method used an atomic emission detector (AED) adjusted to detect the sulfur in the substances that eluted from the column. The average results of the analyses for the HETM are shown in **Table 4B-5.**   Since it has been shown that the HD has nearly all been converted to products, the other portion, 3 to 21 mole percent, must have been converted to other products. Besides the linear product, HEAES, the GC/AED technique indicated the presence of many trace-level chlorine-containing substances.   The 1,4-dithiane was also quantitatively determined by the GC/AED and the ^{13}C NMR methods of analysis. The results indicated that of the 1.0 percent of 1,4-dithiane in the HD used, approximately 80 percent (based on the GC/AED and the ^{13}C NMR results) remained unchanged in the neutralent product.

The characteristics of the neutralent obtained in this process and the results of the Toxicity Characteristic Leaching Procedure (TCLP) analysis are presented in **Appendix 4A** of this permit application.

6   DETOXIFYING GB

MEA-water will also be used as the reagent to detoxify GB during the MMD-1 test, but a lower concentration of MEA in the mixture (lower than that used for HD) will be used. A mixture of MEA:water of 45:55 ratio will be used because this composition has been found to be effective and also avoids an undesirable viscous product solution (Patel et al., 1995b). If only 10 percent water is present in the reagent, the product solution was found to be quite viscous.

Formation of Agent Q and EDC

2 S
$\diagup$ CH$_2$CH$_2$Cl
$\diagdown$ CH$_2$CH$_2$Cl

HD

$\longrightarrow$

CH$_2$ — S—CH$_2$CH$_2$Cl
CH$_2$ — S—CH$_2$CH$_2$Cl

Agent Q

$+$

Cl—CH$_2$CH$_2$—Cl

EDC

Formation of 1,4-Dithiane and EDC

CH$_2$ — S—CH$_2$CH$_2$Cl
CH$_2$ — S—CH$_2$CH$_2$Cl

Agent Q

$\longrightarrow$

S $\bigcirc$ S

1,4-dithiane

$+$

Cl—CH$_2$CH$_2$—Cl

EDC

Reaction of Q with MEA

CH$_2$ — S—CH$_2$CH$_2$Cl
CH$_2$ — S—CH$_2$CH$_2$Cl

Agent Q

$+$ 4 HOCH$_2$CH$_2$NH$_2$

MEA

$\longrightarrow$

CH$_2$ — S—CH$_2$CH$_2$NHCH$_2$CH$_2$OH
CH$_2$ — S—CH$_2$CH$_2$NHCH$_2$CH$_2$OH

MEA-Q

$+$
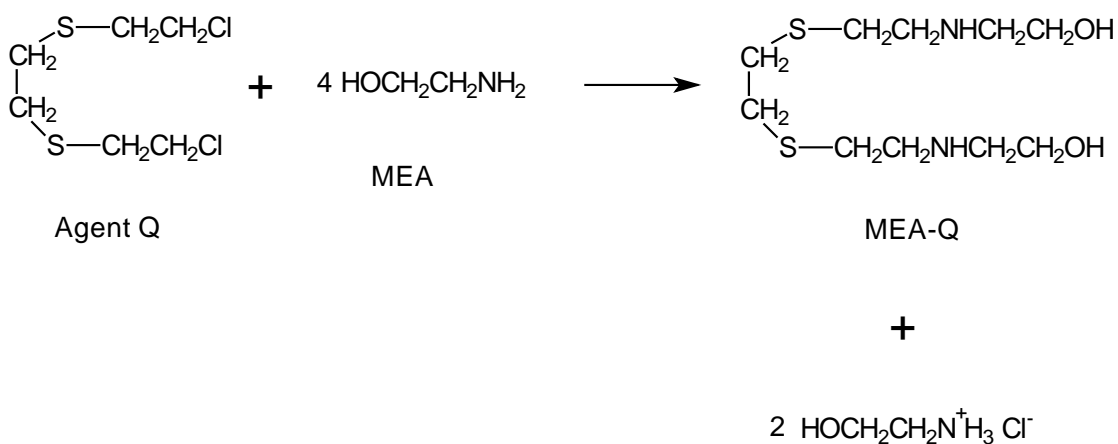
2 HOCH$_2$CH$_2$N$^+$H$_3$ Cl$^-$
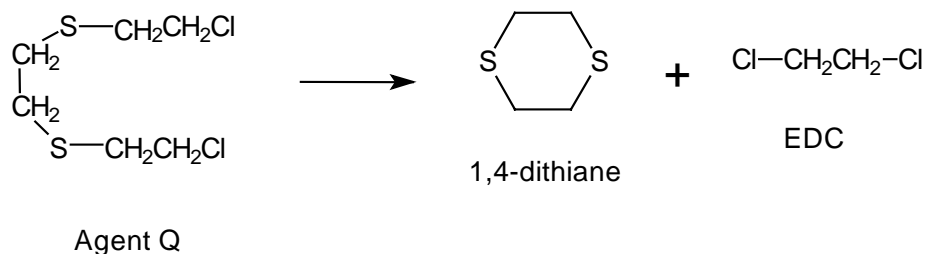
Figure 4B-9. Formation of Q, 1,4-Dithiane, and EDC and Reaction of Q with MEA/Water

**Table 4B-5.   Results of Analyses for N-(2-Hydroxyethyl)thiomorpoline (HETM)
the HD/MEA/Water Neutralent**

Laboratory Runs in 5-Liter Reactor with 9-11 wt% HD in mix		Method of Analysis	Weight % HETM, Range	Mole % Conversion of HD to HETM	
Temperatures Observed	Runs			Average	Standard Deviation
80-210°F	8	GC/AED[a]	6.9 - 8.8	97	5.2
75-150°F	3	GC/AED[a]	6.3-7.5	79	5.6
75-150°F	5	^{13}C NMR[b]	6.7-7.3	80	6.9

NOTES:

a   These two series of results were obtained by different analysts.

b   The average of results from two different analysts.

Laboratory studies (ERDEC, 1996b; Procell et al., 1994) of the reaction of GB with the MEA-water reactants have shown that two organic products, isopropyl methylphosphonic acid (IMPA) and 2-aminoethyl isopropyl methylphosphonate (GB-MEA), are formed along with the inorganic hydrogen fluoride (HF). The two acids will form soluble salts with the MEA, as shown in **Figure 4B-10**. NMR spectroscopy was used to identify and quantitate these products. It was found that of these two products, MEA and IMPA comprised 74 mole percent and GB-MEA amounted to 26 mole percent. After an initial test with 10:1:MEA:water reagent, Patel and coworkers (1995b) examined the use of more dilute MEA (45 volume percent) in water as a reagent and found that the reaction was rapid, even when starting at 60°F, and the products were mobile with viscosities of 2.3 to 3.9 centipoise at 86°F. The results, which are summarized in **Table 4B-6**, also showed that the reaction produced maximum temperatures of less than 100°F even when 100 mL of GB were treated with 1,000 mL of MEA-water (45:55) in a Dewar flask. Analyses of samples taken from the mixture showed that all of the GB was converted rapidly; no GB, above the detection limit of 15 mg/L, was found in samples taken even 1 minute after mixing the reactants. Later studies by ERDEC (1996b) of the reaction products with the use of more sensitive methods of analysis showed that only 12 to 94 mg/L of GB remained after three hours. In these experiments the process was started at 76° to 90°F and the heat of the reaction produced final temperatures of 109° to 126°F. It is not expected that the heat of the reaction will cause any significant increase in the temperature of the reactants in the MMD-1 system. The reactions in the Dewar can be considered to approach an adiabatic condition, so that the heat of reaction per weight of GB treated can be calculated from the observed temperature rise, the quantity of material, and an estimated specific heat of the materials. From the three experiments run in the Dewar (see **Table 4B-6)**, the heat of the reaction was calculated to be 356 Btu/lb (+/-141 Btu/lb) of GB. Therefore, if the GB in a 155-millimeter artillery round, 6.5 lb, is treated with 100 gallons of the MEA/water reagent, it can be estimated that the temperature of the mixture will rise only 3°F.
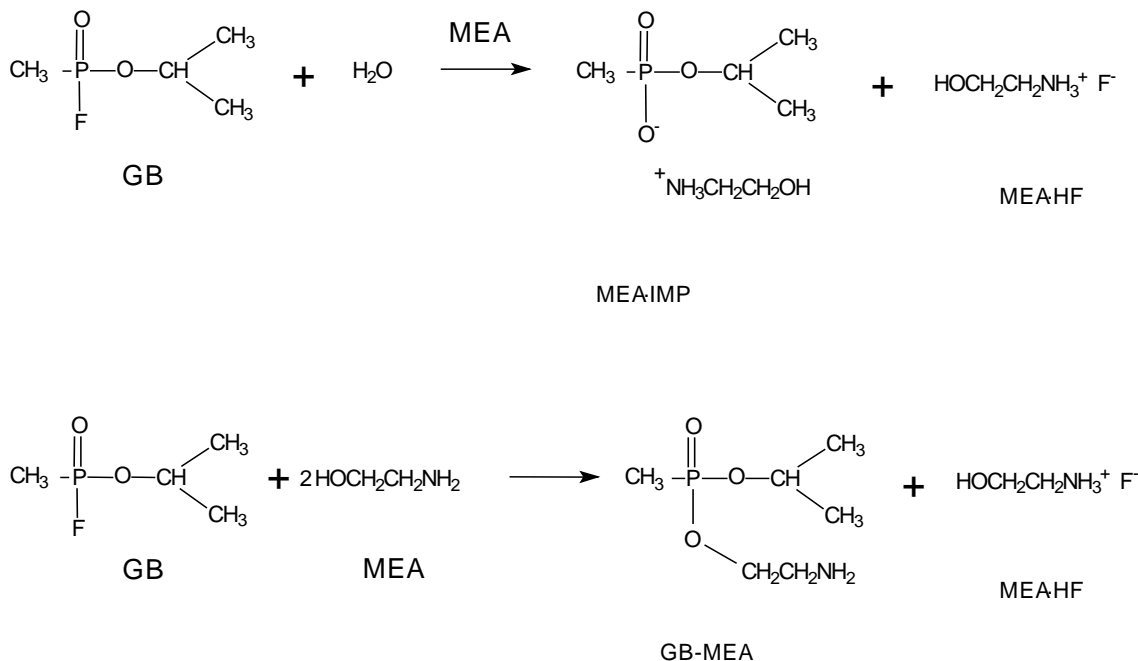
$$CH_3-\overset{\overset{O}{\|}}{\underset{F}{P}}-O-CH\overset{CH_3}{\underset{CH_3}{\big<}} \;+\; H_2O \;\xrightarrow{\text{MEA}}\; CH_3-\overset{\overset{O}{\|}}{\underset{O^-}{P}}-O-CH\overset{CH_3}{\underset{CH_3}{\big<}} \;+\; HOCH_2CH_2NH_3^+\,F^-$$

GB $^+NH_3CH_2CH_2OH$ MEA·HF

MEA·IMP

$$CH_3-\overset{\overset{O}{\|}}{\underset{F}{P}}-O-CH\overset{CH_3}{\underset{CH_3}{\big<}} \;+\; 2\,HOCH_2CH_2NH_2 \;\longrightarrow\; CH_3-\overset{\overset{O}{\|}}{\underset{\underset{CH_2CH_2NH_2}{O}}{P}}-O-CH\overset{CH_3}{\underset{CH_3}{\big<}} \;+\; HOCH_2CH_2NH_3^+\,F^-$$

GB   MEA   MEA·HF

GB-MEA

Figure 4B-10. Reaction of GB with MEA/Water

Table 4B-6. Adiabatic Reaction of GB with MEA/Water (45:55)

GB:Reagent Volume Ratio	Initial Temp. F	TemperatureRise, F	Minutes to Max Temperature	Product Viscosity at 86 F
1:10[a]	59.6	35.5	1.9	3.9
1:20[a]	58.6	31.4	3	2.6
1:30[a]	64.7	10.2	8	2.34
1:9.1[b]	88	33	5.5	NM
1:9.1[b]	90	32	5.5	NM
1:9.1[b]	94	32	5.0	NM
1:9.1[b]	89	30.5	4.0	NM
1:10[b]	76	33	4.5	NM
1:9.1[b]	77	32	4.0	NM
1:9.1[b]	76	33	4.0	NM

NOTES:

a In these experiments, a measured volume of GB was first cooled to 60 F. The cooled GB was then added, within 5 seconds, to 1,000 mL of a 60 F-stirred solution of 45 percent by volume MEA in water in a Dewar flask. The temperature was measured and recorded every 0.5 seconds with a thermocouple.

b These experiments were run using a jacketed, 5-liter reactor; the jacket was filled, but not heated. A weighed amount of GB (363 to 366 g or 329 to 332 mL) was added to 3,650 g. (3,650 mL) of 45% MEA in water over a period of 4 to 5 minutes.

The GB neutralents from four experiments were stored at 39°F for 23 to 31 days, and then analyzed repeatedly for the concentration of GB. As shown in **Table 4B-7**, the GB concentration had been reduced to less than 352 ppb in all the samples; a week later the GB was less than 203 ppb; and after 46 days, analysis of the neutralent from the first run showed no detectable amount of GB. The limit of quantitation was calculated to be 25 ppb, based on lowest GB standard used. This standard produced a signal that was 14 times greater than the instrument noise (ERDEC, 1996b). GB added to the neutralent at this level could not be detected.

In the laboratory tests of GB neutralization, a munitions grade of GB was used. The analysis for GB by GC/thermal conductivity detector (TCD) and analysis for the other components by GC/MS is shown in **Table 4B-8**. Quantitative ^{31}P NMR analyses of four neutralents obtained in laboratory runs from the treatment of GB with MEA/water were performed. A weighed amount of an internal standard, triethyl phosphate, was added to each sample before analysis to allow the calculation of the weight percent of the phosphorus-containing components. The average concentrations of the four samples are shown in **Table 4B-9**. Because the GB initially added to the MEA/water reagent amounted to 9.1 percent of the total in each of the four runs, the mole percent conversion can be calculated from the phosphorus-containing components and the chemical stoichiometry of the reactions. In **Table 4B-9**, the mole percent conversions of GB to IMPA and the isopropyl 2-aminoethyl methylphosphonate, GB-MEA in **Figure 4B-9**, are shown. The total accounts for 95 mole percent of the starting GB. The ^{31}P NMR method also demonstrated that 95 percent of the phosphorus-containing materials in the GB used could be accounted for in the neutralent product.

The characteristics of the GB neutralent obtained in this process and the results of the TCLP analysis are presented in **Appendix 4A** of this permit application.

Table 4B-7. Residual GB Found in the Neutralent from the GB/MEA/Water Reaction

Experiment No.,MRCS-GB-	Days Stored at 39°F Before Analysis	Replicates analyzed	Concentration of GB by GC/MSD Method ppb (Standard Deviation)
2.5	23	3	352 (+/-10.1)
2.5	31	1	180
2.4	29	3	338 (+/-7.1)
2.4	37	1	180
2.3	30	3	326 (+/-7.1)
2.3	38	1	203
2.2	31	7	340 (+/-15.4)
2.2	39	1	203
2.2	46	3	none detected (<25 ppb)

Table 4B-8. Composition of the Munitions Grade GB Used in the MEA/Water Neutralization

Component	Percent Found
GB	86.4[a]
Diisopropyl methylphosphonate (DIMP) [Production impurity[c]]	8.6[b]
Tributylamine [stabilizer[d]]	2.3[b]
Diisopropylcarbodiimide, diisopropylurea and -thiourea [stabilizer & products[d]]	1.1[b]
Other methylphosphonate fluoridates	0.8[b]
Ethyl isopropyl methylphosphonate and other esters [production impurities[c]]	0.7[b]
Other organic components	0.09[b]

NOTES:
a   A result of the GB purity determination by GC/TCD method in area percent, average of three runs.
b   The GC mass selective detector (MSD) results of the analysis of GB. The results in area percent have been scaled so that the impurities plus the GC/TCD result equals 100 percent. Other non-volatile impurities may be present in this lot of GB, since the methods of analysis applied would not determine such compounds.
c   The impurities were formed during the manufacturing of the GB.
d   These components are stabilizers added to the GB and the products formed from those stabilizers upon storage.

Table 4B-9.   Product Distribution in the GB/MEA/Water Neutralents from Four Laboratory Runs Average of the Four ^{31}P NMR Quantitative Analyses

Product Found	Mole % Conversion of GB to Product	Average Conc. Found Wt. Percent
Isopropyl methylphosphonic acid (major product; present as an MEA salt[a]) (IMPA)	71	5.50
Isopropyl 2-aminoethyl methylphosphonate (a major product)	24	2.46
Diisopropyl methylphosphonate (impurity in the GB)	N/A[b]	0.39[b]
Methylphosphonic acid (present as the MEA salt[a], a hydrolysis product) (MPA)	N/A[b]	0.06[c]

NOTES:
a   All of the phosphonic acids will be present in the neutralent as salts of MEA because they are relatively strong acids. The concentrations in this table are listed as the acids; the salts will be 1.31 or 1.63 times as great for the IMPA and MPA salts, respectively.
b   This impurity would be present at 0.78 percent if none of it were converted. N/A: not applicable.
c   The methylphosphonic acid is assumed to form only from the 0.06% methylphosphonic difluoridate in the GB; more may be formed by hydrolysis of the IMPA.

7   DETOXIFYING PHOSGENE

Phosgene may be found in some recovered munitions at certain storage sites. For the test phosgene will be purchased from industrial suppliers. The munition treatment vessel (MTV) will be first pressurized to 20 pounds per square inch gauge (psig) with nitrogen before the phosgene is introduced into the reactor vessel. When the phosgene is released into the reactor vessel, the phosgene will not boil but will remain as a liquid if the temperatures are below 93°F. The temperature is maintained below 93°F by a thermostat, but if it should fail a small amount of the phosgene will evaporate to reduce its temperature. The liquid and gas released from these cylinders will be converted to nearly nontoxic products by treating them with a 20 weight percent sodium hydroxide solution in water. In this reaction, the phosgene is rapidly converted to sodium carbonate and sodium chloride, as shown below.

$$COCl_2 \;\; + \;\; 4NaOH \;\; \rightarrow \;\; Na_2CO_3 \;\; + \;\; 2NaCl \;\; + \;\; 2H_2O$$

Three cylinders containing the quantities of phosgene listed in **Table 4B-3** will be breached in the MTV, and the liquid and gas will be treated in the liquid-waste system, and in the gas-processing system. From the heats of formation of all of the reactants and products of the reaction (Dean, 1985), it was calculated that approximately 1,940 Btu/lb of phosgene would be released in this reaction. From this value, the amount of heat that each quantity of phosgene would generate in processing was calculated, and the results are shown in **Table 4B-10**.

Since 2,288 pounds (225 gallons) of sodium hydroxide solution are expected to be used (specific heat: 0.835 Btu/lb/°F, Perry and Green, 1984), the temperature could rise by the maximum values shown in **Table 4B-3** if no heat is lost from the solution to the equipment. For the largest quantity of phosgene treated, the temperature rise of 73°F is significant and should be avoided. Therefore, when such larger amounts of phosgene are treated, they will be combined slowly with the reagent in the liquid-processing system.

Also, if excess phosgene is added to the sodium hydroxide solution then carbon dioxide gas may form, as shown below:

$$COCl_2 \;\; + \;\; 2NaOH \;\; \rightarrow \;\; CO_2 \;\; + \;\; 2NaCl \;\; + \;\; H_2O$$

Table 4B-10. Potential Phosgene Test Items

Item No.	Phosgene, lb (gal)	Calculated Heat Generated, Btu	Temperature Rise, for Liquid Only
Cylinder #1, #2	3.15 (0.26)	6,111	3°F
Cylinder #3, #4	11.9 (1.0)	23,086	12°F
Cylinder #5, #6	71.4 (6.0)	138,516	73°F
4.2-in. mortar round	6.25 (0.53)	12,125	6°F

Although the CO_2, which would increase the vessel pressure, will react further with sodium hydroxide, as shown below, it will have to be absorbed from the gas phase into the liquid. This latter process is expected to be slower than the liquid-solution reaction.

$$CO_2 \;\; + \;\; 2NaOH \;\; \rightarrow \;\; Na_2CO_3 \;\; + \;\; H_2O$$
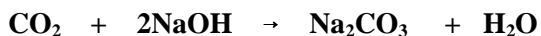
It is expected that removing small amounts of phosgene gas from the system will require the most time in the phosgene detoxification process. Earlier studies (Mirabella, 1976) show that phosgene requires at least two absorbers filled with sodium hydroxide solution to absorb and react all of the phosgene in the gas phase. The phosgene vapors will be removed in the liquid processing, gas-processing, and waste gas-processing systems.

Based on the process description above, the detoxified liquids from the phosgene treatment are expected to contain only sodium hydroxide, sodium carbonate, sodium chloride, and water. The actual composition of the waste generated will be determined during the MMD-1 Test.

8   DETOXIFYING VX

Process development studies to date have determined that sodium hydroxide in MEA will effectively detoxify VX (ERDEC, 1996c; Bartram et al., 1994). The reagent is prepared by mixing one volume of 50 percent aqueous sodium hydroxide (NaOH) with nine volumes of MEA. In this mixture, the hydroxide ion and the 2-aminoethoxide (*1*) ion are expected to be present, as shown by the equilibrium below. With several reagents, studied earlier, VX often forms highly toxic by-products, or high-process temperatures are required; the sodium hydroxide-MEA (NaOH/MEA/water) is expected to avoid these problems. This

$$HOCH_2CH_2NH_2 \; + \; Na^+ {}^-OH \; \rightleftharpoons \; Na^+ {}^-OCH_2CH_2NH_2 \; + \; H_2O$$

MEA   *1*
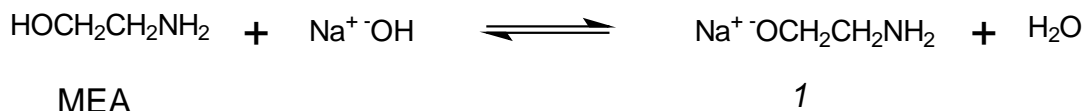
process has been studied by ERDEC (Bartram et al., 1994; Lindsay, 1995; ERDEC, 1996). The reaction mixture is heterogeneous (the VX is not completely soluble in the reactant mixture), and the small-scale studies showed that the VX was completely converted to products within an hour if the mixture was heated to 140°F (60°C) (Bartram et al., 1994). The most recent studies have shown that at least 99.996 percent of the VX added to the reagent was converted to products in less than 110 minutes if the temperature is maintained at 113-125°F (ERDEC, 1996c). If the temperature is below 90°F, VX, at 10 mg/L or greater concentrations, can persist for 180 minutes. After the latter mixture is heated for another 72 minutes, the VX concentration is reduced to below 2 mg/L. The 125°F temperature has been shown to be important. A laboratory experiment of VX neutralization with NaOH/MEA/water at 115°F (46°C) for 22 hours produced a mixture in which 60 mg/L of VX remained after 22 hours of stirring (Lindsay, 1995), and at 77°F (25°C), 0.9 percent of the original VX concentration remained after 23 hours of stirring. Based on these results, 125°F NaOH/MEA/water reactant must be rapidly mixed for at least an hour to complete the conversion of the VX.

The products of the laboratory experiments on the neutralization of VX with NaOH/MEA/water were analyzed by NMR, and GC/MSD and GC/infrared detector (IRD) methods (ERDEC, 1996c). From these results it was determined that the major products of the reaction result from the replacement of the 2-diisopropylaminoethylthio (DIPAE-THIO) group in the VX. The hydroxide ion replaces the DIPAE-THIO group to form ethyl methylphosphonic acid and the DIPAE-THIO ion. The MEA ion, *1*, also simultaneously replaces the DIPAE-THIO group to probably form O-ethyl O=(2-aminoethyl) methylphosphonate as an intermediate (VX/MEA intermediate in **Figure 4B-11**). The intermediate apparently is hydrolyzed rapidly to the O-(2-aminoethyl) methylphosphonic acid (AEMPA). Either the EMPA or the AEMPA can be further hydrolyzed to form the dibasic methylphosphonic acid. All of the acids, which may be considered intermediates, will be converted to salts by the excess sodium hydroxide that is present in the solution to form the products shown in **Figure 4B-12**. By quantitative ^{31}P NMR analysis, the concentration of the major phosphorus-containing products in the neutralent were determined (ERDEC, 1996c). These concentrations are shown in **Table 4B-11**, along with the molar conversion of

the VX to each product. In this calculation, the other phosphonates and pyrophosphonates, present as impurities in the VX, are included because they will also be converted to the phosphonate salts shown. The NaTHIOL is assumed to also be a co-product formed by the substitution reaction (see **Figure 4B-12**). The THIOL was identified by NMR analyses and GC/AED and GC/IRD techniques, but it could not be quantitatively measured.
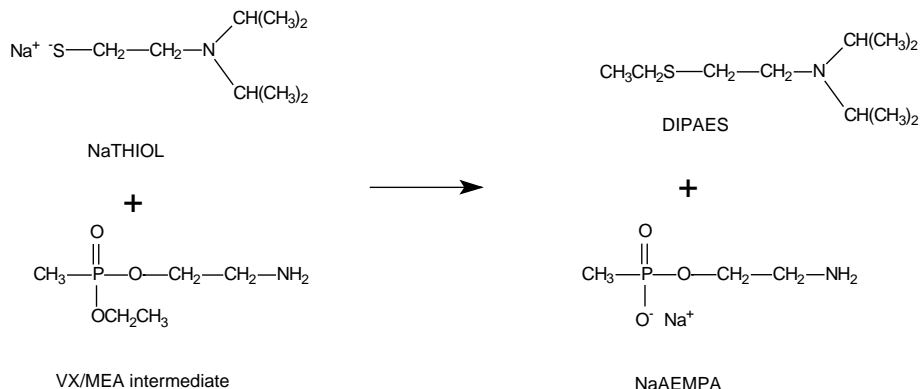

Figure 4B-11. Proposed Reaction to form 2-Diisopropylaminoethyl Ethyl Sulfide

Table 4B-11. Phosphorus-Containing Components in VX Neutralent[a]		
Compound[b]	Mole % of Total Phosphorus Charged[c]	Weight Percent of the Compound in the VX Neutralent[d]
NaEMPA: sodium ethyl methylphosphonate	43.5	2.0
NaAEMPA: sodium O-(2-aminoethyl) methylphosphonate	35.4	1.8
Na$_2$MPA: disodium methylphosphonate	11.2	0.5
Other phosphorus compounds	6.5	very low[e]
Unaccounted for by analysis	3.4[f]	unknown[f]

NOTES:

a   These data were calculated from the NMR analyses of VX neutralent prepared from 9.37 parts of VX to 100 parts of reagent (85.7 parts MEA:14.3 parts of 50% NaOH/H$_2$O).

b   The phosphonates were reported as acids by the analyst (ERDEC, 1996c); the concentrations as acids were converted to the concentrations as salts. The structures of these products are shown in **Figure 4B-12.**

c   The molar percents were calculated from the moles of the phosphorus-containing constituents in the VX (0.3676 moles/100 g.), and the amount of the VX charged into the neutralent, 8.569 g. VX/100 g. neutralent (see ERDEC, 1996c) and the weight percent of the products found.

d   The concentrations were found to be precise to within 1.2-3 percent expressed as relative standard deviation.

e   Some unidentified peaks appeared in the ^{31}P NMR spectra; these amounted to 6.5 percent of the total phosphorus; without the identity the weight percent could not be calculated.

f   From the NMR results it was determined that 96.6% (+/-0.8%) of the phosphorus was accounted for as compounds in the neutralent.
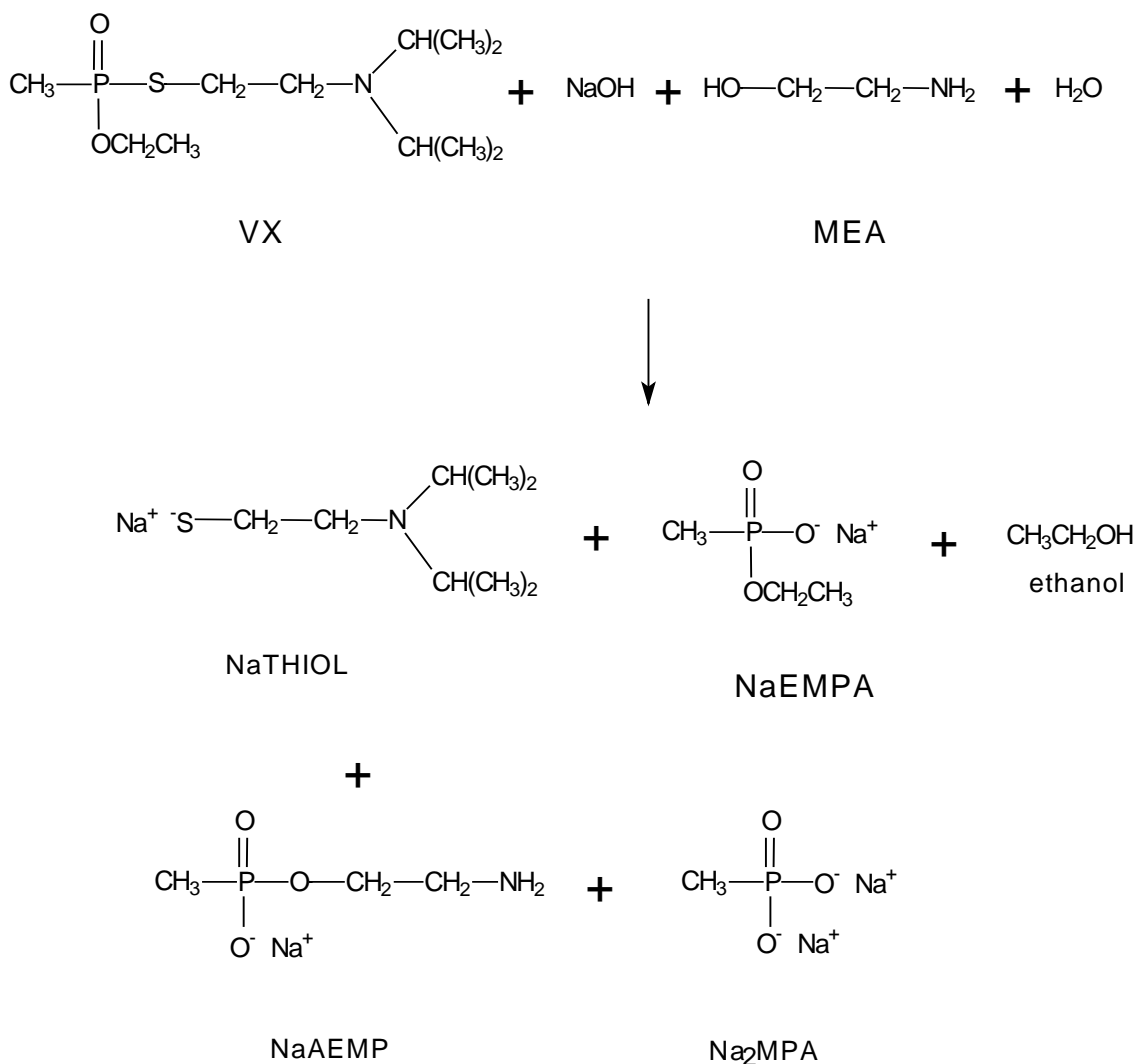
Figure 4B-12. Major Product from Reaction of NaOH/MEA/Water with VX

Several other products were found in the VX neutralent; these must be present at levels of no more than 4 percent total. Three sulfides/disulfides were identified, and it was proposed that these were formed as shown in **Figures 4B-11** and **4B-13**. The munitions grade VX is stabilized with 0.02 to 4+ percent of either dicyclohexylcarbodiimide or diisopropylcarbodiimide. These carbodiimides are expected to be hydrolyzed in the NaOH/MEA/water reagent to form the corresponding 1,3-dicyclohexyl- or 1,3-diisopropylurea as shown in **Figure 4B-14**. In the laboratory-prepared neutralent, cyclohexylamine was identified; this product may have resulted from the hydrolysis of the 1,3-dicyclohexylurea as shown in **Figure 4B-14**. Another minor component has been identified as sodium N-(2-hydroxyethyl) methylphosphoramidate (PN-MEA), which could be formed from MEA sodium salt and VX as shown in **Figure 4B-15**. Ethylene glycol and 2-diisopropylaminoethanol were also found in the VX neutralent (ERDEC, 1996c).
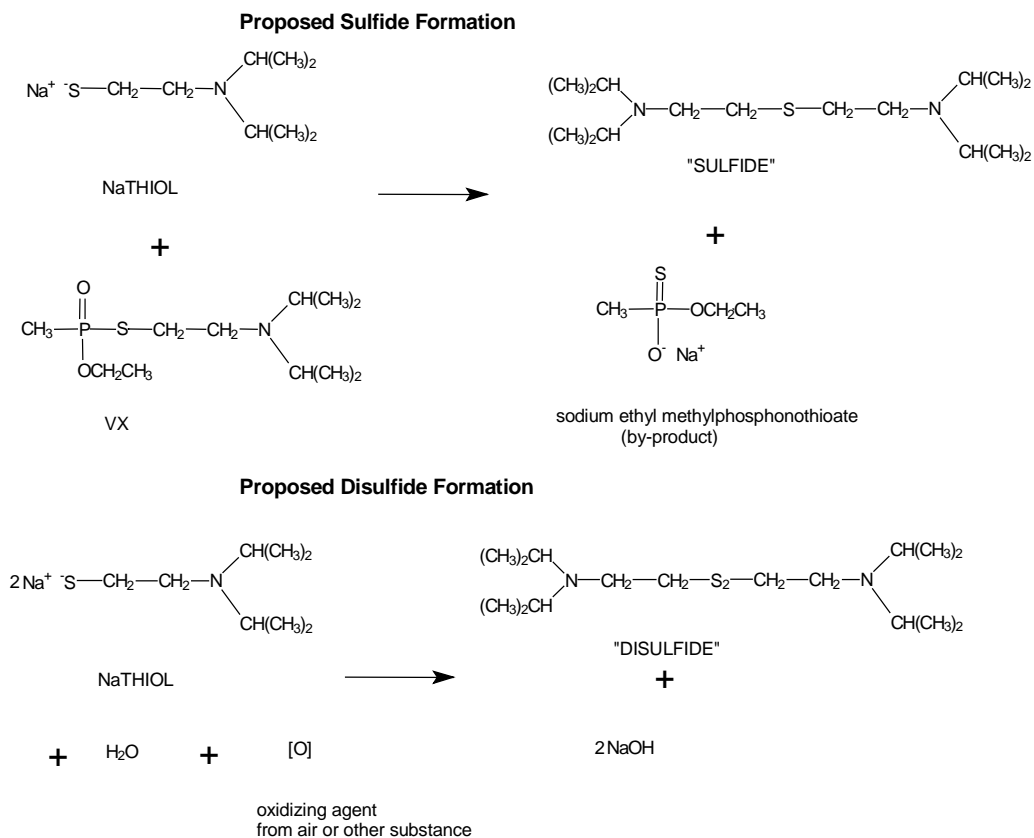
Proposed Sulfide Formation

NaTHIOL

+

VX

"SULFIDE"

+

sodium ethyl methylphosphonothioate
(by-product)

Proposed Disulfide Formation

NaTHIOL

"DISULFIDE"

+

+ H$_2$O + [O]

2 NaOH

oxidizing agent
from air or other substance

**Figure 4B-13. SULFIDE and DISULFIDE Formation in the
VX/NaOH/MEA Neutralization Process**

dialkylcarbodiimid

1,3-dialkyl

1,3-

2

cyclohexylamin
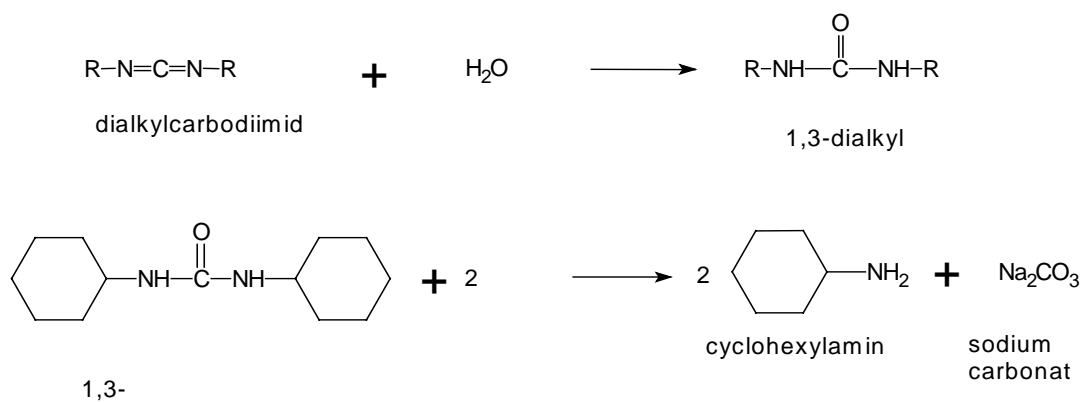
sodium
carbonat

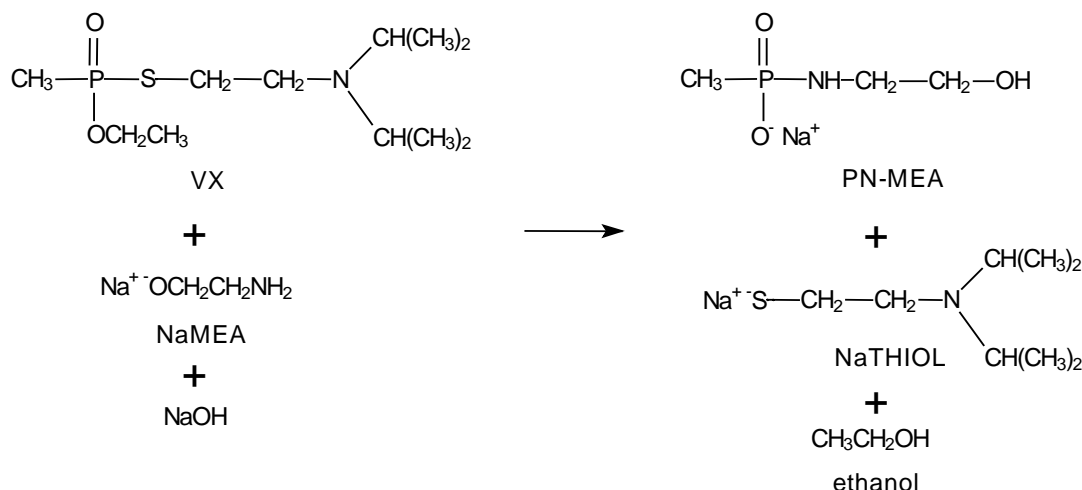**Figure 4B-14. Formation of 1,3-Dialkylureas and Cyclohexylamine**

**Figure 4B-15. Formation of Sodium N-2-hydroxyethyl Methylphosphoramidate
from VX/NaOH/MEA/Water**

If VX is treated with sodium hydroxide in water solution, 10 to 15 percent of the VX is converted to a nerve toxic compound, sodium S-(2-diisopropylaminoethyl) methylphosphonothioate (EA 2192, sodium salt), as shown in **Figure 4B-16**. In some previous work (ERDEC, 1996c), measurable levels of EA 2192 had been found when VX was neutralized with NaOH/MEA/water solutions. No significant concentrations of the EA 2192 salt were found by LC/MS or ^{31}P methods of analyses that were applied to the VX neutralents obtained in the recent studies (ERDEC, 1996c). The analysts estimated that their detection limit for EA 2192 was 10 to 100 ppm, but they did not definitely establish a detection limit.

9   PRECISION AND ACCURACY OF THE CHEMICAL AGENT METHODS OF ANALYSIS

The method of analysis for each residual agent in the neutralent obtained from the detoxification of that chemical agent must be reliable and accurate to ensure that the method will work adequately. The Army=s laboratory, ERDEC, and U.S. Army contractors have studies of methods of analysis in progress that meet precision and accuracy criteria. These criteria require testing the method repeatedly over a 4-day period.
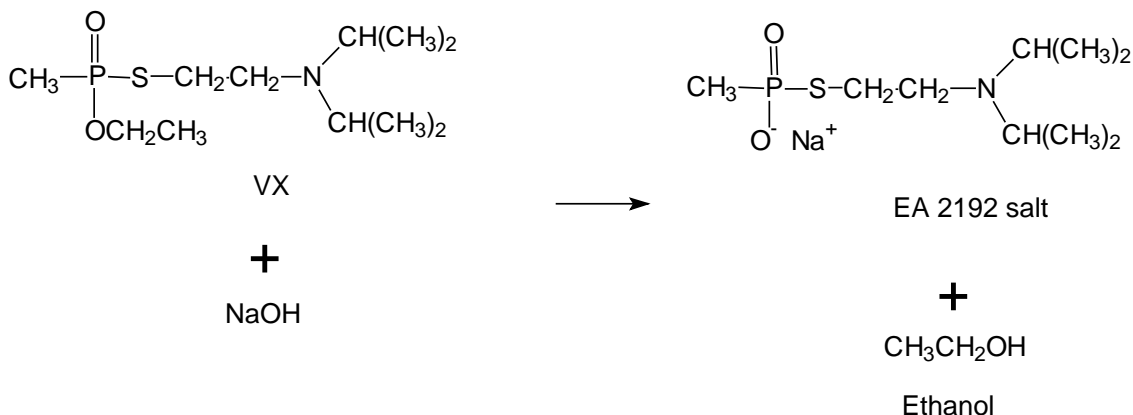

Figure 4B-16. Formation of Sodium S-(2-diisopropylaminoethyl) methylphosphonothioate

ATTACHMENT 4B-1
REFERENCES

ATTACHMENT 4B-1
REFERENCES

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